



Separation of manganese, zinc and nickel from leaching solution of nickel-metal hydride spent batteries by solvent extraction

Valentina Innocenzi, Francesco Veglio*

Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università degli Studi dell'Aquila, 67100 Monteluco di Roio, L'Aquila Italy

ARTICLE INFO

Article history:

Received 23 April 2012

Received in revised form 18 July 2012

Accepted 7 August 2012

Available online 14 August 2012

Keywords:

NiMH spent batteries

Base metals

Solvent extraction

Cyanex 272

D2EHPA

ABSTRACT

The paper is focused on the use of solvent extraction for purification of leach liquor solutions obtained by leaching of NiMH spent batteries: dissolved nickel is separated from manganese and zinc by liquid–liquid extraction using D2EHPA. Two extractants were investigated: D2EHPA and Cyanex 272 in *n*-dodecane, and the preliminary tests suggested that D2EHPA is more efficient to separate Mn and Zn from the leaching solutions. Under the optimized conditions it is observed that in extraction circuit a recovery >99% of zinc and >95% of manganese is achieved. The experimental results suggested that two cross-flow liquid–liquid extraction steps are adequate to extract 100% of Zn and about 95% of Mn while the residual Ni was about 80% of its initial content. The extracted elements are stripped using a 4 M sulfuric acid solution and the stripping yields were very high, >99% for Ni and Zn and about 98% for Mn. Finally, a possible process flowsheet to separate Mn and Zn from leach liquor of NiMH spent batteries by solvent extraction is proposed. The process includes two stages of extraction with 20% v/v of D2EHPA in *n*-dodecane ($O/A = 1/1$, room temperature, 30 min of contact, $pH \leq 2.5$) and one stage of stripping with 4 M of H_2SO_4 ($O/A = 1/0.5$, room temperature, 15 min of contact). The raffinate rich in Ni has the following composition: 32 g/L of Ni, 0.87 g/L of Mn, and the aqueous liquid from the stripping step had the following concentrations: 9.86 g/L of Zn, 18 g/L of Mn and 7.33 g/L of Ni. The first solution could be treated to recover Ni, for example by precipitation, whereas the second liquid could be recycled in electrolytic section to recover metallic zinc and manganese oxide.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Solvent extraction is one of the most efficient methods used to remove, separate and concentrate metallic species from aqueous media. The use of liquid–liquid extraction technology in industry has increased rapidly since 1970, and in the last 10 years there have been incremental advances in the application of SX to hydrometallurgy. A very large number of extractants are available for use in hydrometallurgy with more than 40 reagents (including Cyanex 921, Cyanex 272, D2EHPA, MIBK, TBP, TOPO, etc...), (Flett, 2005; Ritcey, 2006). Solvent extraction in hydrometallurgical processes is used to separate the various metals and numerous studies have been carried out to study the dynamics of base metal extraction and this technology has been proposed for purification of solutions obtained by processing of ores and waste treatment, such as spent catalyst, spent batteries and other wastes. The following articles describe liquid–liquid extraction of metals such as Ni, Mn and Zn from sulfate media using different extractants.

Devi et al. (1997) studied solvent extraction of zinc and manganese from sulfate solutions using NaCyanex 272. The authors observed that the percentage of extraction of metal ions increased

with increasing equilibrium pH and linearly with increasing extractant concentration up to 0.05 M.

Reddy et al. (1999) described a process to extract Ni using PC-88 A in kerosene. More than 99% of nickel was extracted in three stages with 1 M of extractant neutralized to 50% at O/A ratio (organic phase volume/aqueous phase volume) of 2.2. Ni was stripped in two steps at the O/A ratio of 5 with H_2SO_4 ; Mn yield of stripping was >99.98%.

Kongolo et al. (2003) considered Co and Zn recovery from copper sulfate solution (containing 1 g/L Co^{2+} , 2 g/L Cu^{2+} , 12.60 g/L Zn^{2+} and 8.4 g/L Fe^{2+}) by solvent extraction. Copper was recovered with LIX 984 and stripped using H_2SO_4 . After iron precipitation with $CaCO_3$, Co and Zn were extracted with D2EHPA and separated by stripping with H_2SO_4 . More than 95% Cu, 90% Co and 90% of Zn were recovered.

Tsakiridis and Agatzini (2004) studied extraction of cobalt and nickel from sulfate solutions by 20% Cyanex 301 diluted in Exxsol D-80 with 5% TBP. Co and Ni could be extracted in one stage at $pH = 2$, $T = 50^\circ C$ and O/A ratio of 1. After scrubbing to remove manganese which was co-extracted, Co and Ni were stripped from organic phase by 5 M of HCl (99.6% stripping yield for Co and 99.2% for Ni) in one stage at $T = 50^\circ C$ and O/A ratio of 2. The same authors (Tsakiridis and Agatzini, 2005) investigated the extraction of aluminum in the presence of Co, Ni and Mg from sulfate solutions by 20% Cyanex 272 in Exxsol D-80, with 5% TBP. 99.5% of Al was extracted in a single step at $pH = 3$, $40^\circ C$ and O/A ratio of 1. Co and Mg were extracted

* Corresponding author.

E-mail address: valentina.innocenzi1@univaq.it (F. Veglio).

from organic liquid by scrubbing with water, and 99.6% of Al was stripped by 2 M of H_2SO_4 in a single stage at $T = 40^\circ\text{C}$ and O/A ratio of 2:1.

Reddy and Priya (2005) studied the extraction of Cu, Ni and Zn from sulfate solutions using LIX 84I. The extraction behavior demonstrated that LIX 84I was an efficient extractant for selective separation of metals investigated. They developed a flowsheet to separate metals with extraction and stripping efficiencies >99.5%.

Long et al. (2010) studied the extraction of zinc from sulfate solution using D2EHPA in sulfonate kerosene. Leaching solution of zinc ore contained 18,700 mg/L of Zn and 30 mg/L of ferric ions. The extraction of Zn increased with increasing of pH, volume fraction of D2EHPA and O/A ratio. In a single stage under the condition of equilibrium pH of 2, 20% D2EHPA, O/A ratio of 1, 8 min of contact, 200 rpm and settling time of 10 min, the extraction yield of Zn was ~38%. Under the same conditions the extraction yield was 75% using saponified D2EHPA. Zn was stripped from ferric ions using 196 g/L of H_2SO_4 and 88.60% zinc ion and 1.76% ferric ion were recovered.

The solvent extraction technology is widely used to recover metals from different kinds of waste (i.e. electronic devices, spent catalysts, spent batteries). NiMH spent batteries represent an important source of metals that can be recovered. These batteries consist of a nickel metal hydride negative electrode and a nickel hydroxide positive electrode. Anode, used as hydrogen storage, constituted by alloy based on mischmetal (mainly Ce, La). Recycling of NiMH spent batteries reduces the environmental impact and it is also important for valorization of secondary raw materials (for example rare earths, nickel). Many processes were developed to treat these wastes. Generally speaking, the hydrometallurgical processes provide leaching of NiMH spent batteries with different kind of acids and further recovery of rare earths and other metals by precipitation or solvent extraction technology. Various hydrometallurgical treatments for recycling of NiMH spent batteries foresee a liquid–liquid extraction to recover metals (Fontana and Pietrelli, 2009; Li et al., 2009; Rodrigues and Mansur, 2010; Zhang et al., 1998, 1999).

Zhang et al. (1998) utilized a leaching process with hydrochloric solutions (2 M) at 95°C for 4 h and RE were precipitated with oxalic acid and calcined after a solvent extraction step with 25% D2EHPA in kerosene ($\text{pH} = 2$) and stripping RE from the organic phase with HCl (2 M). After this step oxalic acid was added for RE precipitation. They also recovered nickel and cobalt by solvent extraction with 25% TOA in kerosene, stripping cobalt with HCl (0.01 M) and precipitated Co and Ni as oxalates. Total recovery of RE reached around 98%, whereas total yields of Co and Ni were about 98% and 99.9%, respectively. Zhang et al. (1999) studied another process that involved leaching with sulfuric acid (2 M) at 95°C for 4 h. RE were precipitated as oxalates after solvent extraction, from leaching solutions, with 25% D2EHPA in kerosene ($\text{pH} = 2.5$) and stripped from the organic phase with sulfuric acid (1 M). The process also involved recovery of Ni and Co by solvent extraction with 25% Cyanex ($\text{pH} = 4.1$), stripping with 0.5 M sulfuric acid and precipitation of Co and Ni as oxalates. Total recovery of RE reached 94%.

Li et al. (2009) tested a leaching stage with sulfuric acid (3 M) at 95°C for 4 h, obtaining 5% RE leaching yields. RE were recovered by alkalization with 1 M of NaOH and filtration of the precipitate which was leached again with 1 M of HCl. Recovery of other metals required solvent extraction with 20% of P_2O_4 in kerosene to remove RE, Zn and Fe, scrubbing of Co and Ni with 0.5 M of sulfuric acid and stripping of RE with HCl. Afterwards solvent extraction was carried out at pH 4.5 with 20% Cyanex 272 in kerosene to separate Co from Ni followed by concentration and precipitation of spherical nickel hydroxide. Co was stripped with 1 M of sulfuric acid and concentrated with formation of CoSO_4 .

Fontana and Pietrelli (2009) studied the extraction of individual rare earths from chloride media using HEHEPA in kerosene. The results showed that it was possible to separate the middle RE by 1.0 mol/L HEHEPA. The order of extraction was $\text{Tb} > \text{Gd} > \text{Eu} > \text{Sm}$.

Rodrigues and Mansur (2010) investigated two leaching stages with 8% v/v sulfuric acid and 0% v/v H_2O_2 at 30°C for 1 h. Yields of the first stage were 80–85% for Ni and 95–100% for Co, whereas yields for the second stage were 87% for RE and 100% for Ni. After leaching and filtration, RE were precipitated with NaOH to recover them from the leach liquor. Finally, solvent extraction with 0.5 M D2EHPA ($\text{pH} = 3$) followed by Cyanex 272, >0.6 M ($\text{pH} = 5.7$) separated cadmium, cobalt and nickel from the leach liquor. Total recovery of RE reached around 97.8%.

The present paper describes in detail the experimental tests carried out on pregnant solutions simulating the leach liquors of NiMH spent batteries to separate manganese and zinc from nickel by solvent extraction. The study is part of a research project on the development of a process that treats NiMH spent batteries in sulfate medium and presented in our previous work (Innocenzi and Veglio, 2012). The main features of this previous study were 1) characterization of NiMH spent batteries powder carrying from grinding of NiMH spent batteries by an industrial shredder and a preliminary sieving process; 2) leaching of the powder with sulfuric acid to dissolve metals; 3) recovery of rare earths by selective precipitation.

The previous work showed that the NiMH spent batteries could be leached with sulfuric acid solution and lanthanum and cerium were recovered by precipitation with NaOH; as regard to other metals, contained in leach liquors, this recovery was not efficient. In this present paper solvent extraction is investigated to separate contaminants like Mn and Zn from leaching solutions, so that Ni containing in leach liquor can further be processed for nickel recovery.

2. Material and methods

2.1. Materials

Sulfuric acid (CARLO ERBA, 96%) and citric acid (CARLO ERBA, 99.5%) were used as leaching reagents whereas sodium hydroxide (FLUKA Chemika, $\geq 97\%$) was used for precipitation.

Aqueous pregnant solutions were used for solvent extraction experiments containing nickel, manganese and zinc with similar concentrations of real leaching solutions of NiMH spent batteries. Typical values considered were 40 g/L Ni, 20 g/L Mn and 10 g/L Zn. The solutions for such tests were prepared by dissolution of sulfates in distilled water, in particular nickel sulfate (RIEDEL-DE-HAËN), manganese sulfate (MERCK, $\geq 99\%$) and zinc sulfate (FLUKA, $\geq 99\%$). Sodium hydroxide and sulfuric acid were used to adjust pH. Organic phases were obtained by diluting Cyanex 272 (CYTEC INDUSTRIES BV) or D2EHPA (ALDRICH) in n-dodecane (ALDRICH, 99%).

2.2. Characterization of NiMH spent batteries powder, leaching tests and precipitation tests

Spent NiMH batteries powder was obtained by grinding NiMH spent batteries with an industrial shredder and sieving process and was analyzed by X-ray fluorescence (SPECTRO XEPOS) and atomic absorption spectrometry (VARIAN AA240FS) after chemical attack of the solid samples in order to evaluate percentages of various elements in the powder. Several leaching tests were carried out using grain size <500 μm of the battery powder to determine the best operating conditions. The leach liquors were used to perform precipitation tests with NaOH to investigate the recovery of rare earths and other dissolved metals.

Details of experimental procedures for characterization of spent NiMH powder, leaching and precipitation tests are described in our previous work (Innocenzi and Veglio, 2012).

2.3. Solvent extraction tests

Three series of tests were carried out to define the optimum conditions for zinc, manganese and nickel separation by solvent extraction.

In preliminary experiments the aim was to study extraction of Ni–Mn–Zn and to choose the best extractants between two organic extractants: Cyanex 272 and D2EHPA.

In the second series of tests, several experiments were carried out to investigate the influence of % v/v of D2EHPA in n-dodecane, O/A volume ratio and pH values on extraction yields of metals. Finally, other experiments were performed to examine the number of extraction stages which could be sufficient to purify leach liquors from Mn and Zn. Each test was carried out in separator funnels, at room temperature at desired O/A volume ratio for 30 min. This time was supposed to be sufficient to reach equilibrium between the aqueous and the organic phases: in fact previous tests showed that 5 min were adequate to reach equilibrium. After this time of contact 1 mL of aqueous solution was withdrawn to measure the concentration of Ni, Mn and Zn and the sample was diluted 1:10 with a solution of nitric acid (pH~2) to avoid the precipitation of metals.

2.4. Stripping tests

Two different types of tests were carried out to evaluate the stripping efficiency of sulfuric acid to extract manganese and zinc from the organic phase. The organic liquid from extraction tests contacted with sulfuric acid in separating funnel for about 15 min and then the immiscible liquids were separated and analyzed.

In the first experiment 2 M sulfuric acid solution was used, O/A volume ratio was 1 and four stages of stripping were used. In the second test sulfuric 4 M acid solution was used, O/A volume ratio was 2 with two steps of stripping. For each stage the organic phase containing the extracted metals was mixed with fresh sulfuric acid solution after separation of the two phases.

2.5. Analytical methods

X-ray fluorescence spectroscopy (XRF, SPECTRO XEPOS) method was used to determine metal concentration in solid material samples, while concentrations of Ni, Mn and Zn in the aqueous phase were determined by atomic absorption spectroscopy method (AAS, VARIAN AA240FS). Concentrations of these metals in the organic phases were deducted by subtracting the refined concentrations from initials g/l in the aqueous solutions.

3. Results and discussion

3.1. Precipitation tests

XRF analysis of initial washed powder showed that nickel, manganese and zinc are predominant metals in the analyzed powder (14.3% Mn, 11.7% Ni, 5.30% Zn). Lanthanum and cerium are also found in significant concentration (3.65% La and 1.68% Ce). Results of quantitative analysis by AAS indicate a metal content of about 29% Ni, 13% Mn and 8% Zn. The results of leaching tests permitted to highlight that the most suitable conditions for leaching process were 2 M of sulfuric acid, temperature 80 °C, absence of citric acid and 3 h of leaching time. In these conditions the yields are about 94% for nickel and zinc, 100% for manganese and 35% for lanthanum and cerium. Further leaching experiments suggest that a second stage should be carried out on the solid residue of the first stage for further dissolution of rare earths. The second leach was performed with 1 M sulfuric acid, room temperature, 1 h and 15% pulp density. The first leach liquor has the following concentrations: Ni (~39 g/L), Mn (~19 g/L), Zn (~10 g/L) and other metals in lower quantities as Co (~4 g/L), La (~2 g/L) and Ce (~0.8 g/L). Whereas the second leach liquor contains Ni (~21 g/L), La (~18 g/L), Ce (~8.5 g/L) and Mn (~7.6 g/L). The mix of two liquors has the following composition: ~17 g/L Mn, ~36 g/L Ni, ~10 g/L Zn, ~4.6 g/L La, ~2.1 g/L Ce and ~3.2 g/L Co. As it can be inferred from the literature analysis, a precipitation step is suggested to recover the RE from pregnant solutions.

Addition of NaOH leads to precipitation of RE sulfates starting from pH = 0.7 with the formation of a white solid. Precipitation takes place in a range of pH from 0.7 to 2.0. The rare earths solid precipitates are recovered and characterized by XRF analysis. RE can be selectively recovered from the leach liquor in the pH range 0.7–1.6 adding NaOH to the leach liquor. Recoveries and purities are estimated to be about 95% and 89–91%, respectively.

The leach liquors after RE precipitation are collected in order to carry out a further selective precipitation step. The aim is to evaluate if other base metals could be selectively removed from the leach liquor. Precipitation of base metals is carried out adding further NaOH and investigating larger pH levels: after reaching a pH value the suspension is filtered, the solid recovered and further NaOH is added to reach the next pH level; this procedure was repeated at three times 2, 5 and 7 as pH levels.

Table 1 shows the average concentration and precipitation yields during precipitation test. For Ni, Mn and Zn the % of precipitation are very similar to each other. These trends suggest that it is not possible to selectively precipitate metals in the conditions investigated.

From the solution obtained after RE removal it is possible to collect some rich fraction (with Ni, Mn, and Zn) by selective precipitation. Nevertheless, in order to obtain high purities and base metal separations a liquid–liquid process seems to be necessary.

The details of experimental procedure for characterization of spent NiMH powder, leaching and precipitation tests are described in a previous work (Innocenzi and Veglio, 2012).

3.2. Solvent extraction tests

3.2.1. Preliminary tests and selection of extractants

The first series of test was carried out to investigate the extraction of Ni, Mn and Zn and to choose the more efficient extractant between D2EHPA and Cyanex 272. Metal ions extraction with these organic phases is described by the following theoretical reaction, assuming that the organic species as dimer in alkaline solutions:



where

M metal ions in aqueous liquid;
RH organic species.

The mechanism of extraction considers only the extraction of each metal ion, assuming that:

- the metal species (Zn, Mn and Ni) are divalent ions;
- the mechanism of extraction is described by reaction (3.1), excluding other types of reaction between chemical species;
- the transfer of the metal in the organic phase is not influenced by other metal ions present in the aqueous phase, i.e. it is assumed that there is not co-extraction of metals;
- there is no formation of metal–extractant complexes, undissociated molecules of extractants or molecular of diluents;
- the formation of intermediate complexes not extractable is negligible.

The first test was performed with a solution with concentration close to those obtained after leaching and precipitation step (Innocenzi and

Table 1
Average concentration and % precipitation yields during precipitation tests.

Element	pH = 2		pH = 5		pH = 7	
	g/L	% Precipitation	g/L	% Precipitation	g/L	% Precipitation
Ni	31.76	20.59	25.32	36.68	15.34	61.65
Mn	14.21	28.94	13.05	34.76	11.88	40.58
Zn	7.67	23.31	7.225	27.75	3.28	67.42

Veglio, 2012): about 40 g/L, 20 g/L and 10 g/L respectively for nickel, manganese and zinc. The organic phase consisted of theoretical stoichiometric concentration of D2EHPA (2.42 M) in n-dodecane, in according to Eq. (3.1). The extraction yields of the metals were carried out by adding NaOH and testing larger pH levels: after having achieved the desired pH, the aqueous phase and organic phase remained in contact until equilibrium, and then a sample of aqueous solution was taken and analyzed. After sampling, further NaOH was added to reach the next pH level and this procedure was repeated several times until pH 7.

The influence of pH on the extraction by using D2EHPA in n-dodecane is shown in Fig. 1. The order of extraction is $\text{Zn} > \text{Mn} > \text{Ni}$. At pH 2 all Zn is extracted, whereas 100% Mn extraction occurred at pH 3.5. On the contrary Ni extraction yield remains close to 10% up to pH 3, then increases and at pH about 7 is greater than 80%. From these tests it can be inferred that D2EHPA is very selective for Mn and Zn at low pH.

The maximization of the extraction differences ΔE reported below implies the optimization of the extraction pH:

$$\Delta E_{\text{Zn-Mn}} = E_{\text{Zn}} - E_{\text{Mn}} \quad (3.2)$$

$$\Delta E_{\text{Zn-Ni}} = E_{\text{Zn}} - E_{\text{Ni}} \quad (3.3)$$

$$\Delta E_{\text{Mn-Ni}} = E_{\text{Mn}} - E_{\text{Ni}} \quad (3.4)$$

E refers to the extraction percentage for each pH value. Fig. 2 shows ΔE for various elements. According to this criterion the optimum pH value for separation of Zn from Ni is 2.5. 3–3.5 is the optimum pH found to achieve better separation of Mn from Ni. The separation factors β , that is the ratio of the distribution coefficients, D, for the considered metals ($D = \text{metal concentration in organic phase} / \text{metal concentration in aqueous phase}$) was determined and plotted versus pH in Fig. 3. The highest β values for Zn/Ni are in the range 2–5, increases until pH 3 and then slowly decays. These results suggest that optimization of the separation process of zinc and nickel the pH of solvent extraction is less than 3, these data are similar with the value of the maximum $\Delta E_{\text{Zn-Ni}}$. Two parameters lead to the same optimized solution. The highest β values for Mn/Ni are in the range 3–5, increases until pH 4 and then slowly decays. These results suggest that to optimize the separation of manganese and nickel the pH of solvent extraction is less 4, these data are similar to value of the maximum $\Delta E_{\text{Mn-Ni}}$. Also in this case both parameters lead to the same optimized solution.

The second test was performed with aqueous solution in the same conditions of the first experiment, while the organic phase consisted of theoretical stoichiometric concentration (Eq. (3.1)) of Cyanex 272 (2.42 M) in n-dodecane. For the second preliminary test the influence of pH on the extraction is showed in Fig. 4. The order of extraction is

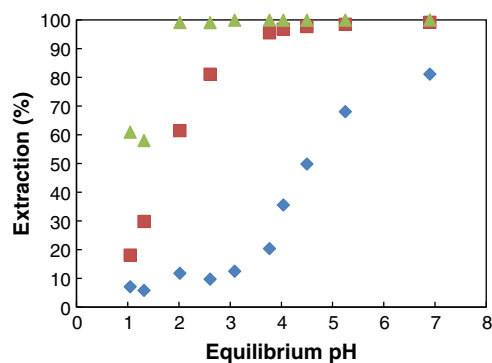


Fig. 1. Extraction efficiency for zinc, manganese and nickel against equilibrium pH during the first preliminary test (initial aqueous phase concentration: 40 g/L Ni, 20 g/L Mn and 10 g/L Zn; O/A = 1, organic phase: 2.42 M D2EHPA in n-dodecane).

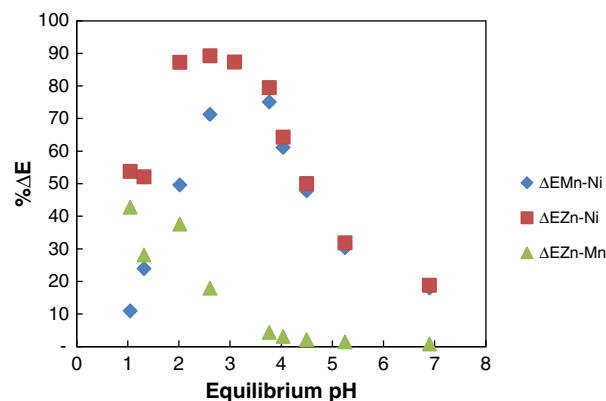


Fig. 2. Extraction differences for various elements in the first preliminary test (initial aqueous phase concentration: 40 g/L Ni, 20 g/L Mn and 10 g/L Zn; O/A = 1, organic phase: 2.42 M D2EHPA in n-dodecane).

$\text{Zn} > \text{Mn} > \text{Ni}$. Zinc is extracted at low pH value (pH = 2), while manganese and zinc are co-extracted at pH > 2. Efficiency increases with pH and the maximum Mn extraction is achieved at pH = 7. Regarding nickel, the extraction yield is only about 40% at pH = 7. Cyanex 272 is very selective for Zn and this result confirms literature data. Figs. 5 and 6 show respectively ΔE for various elements and the separation

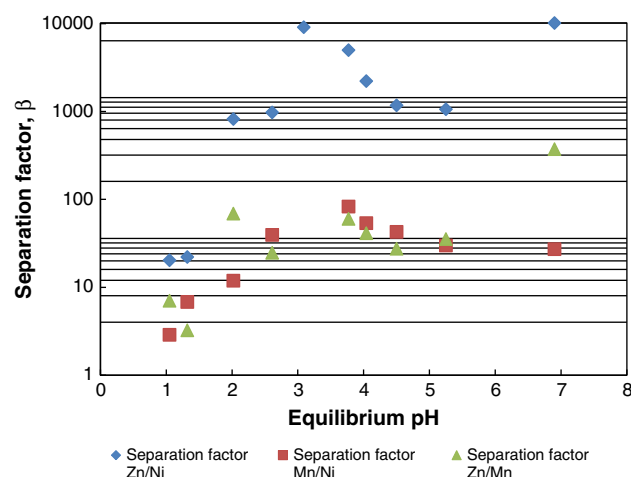


Fig. 3. Separation factors against pH for the first preliminary test (initial aqueous phase concentration: 40 g/L Ni, 20 g/L Mn and 10 g/L Zn; O/A = 1, organic phase: 2.42 M D2EHPA in n-dodecane).

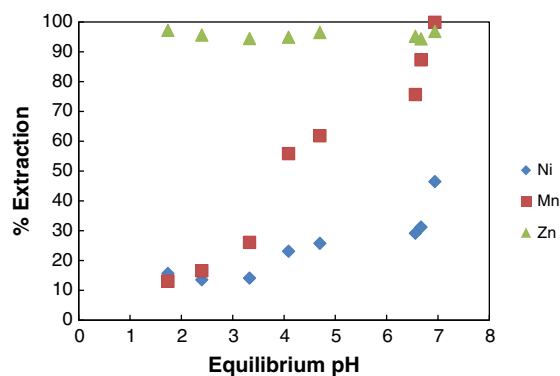


Fig. 4. Extraction efficiency of Ni, Mn and Zn against equilibrium pH during the second preliminary test (initial aqueous phase concentration: 40 g/L Ni, 20 g/L Mn and 10 g/L Zn; O/A = 1, organic phase: 2.42 M Cyanex 272 in n-dodecane).

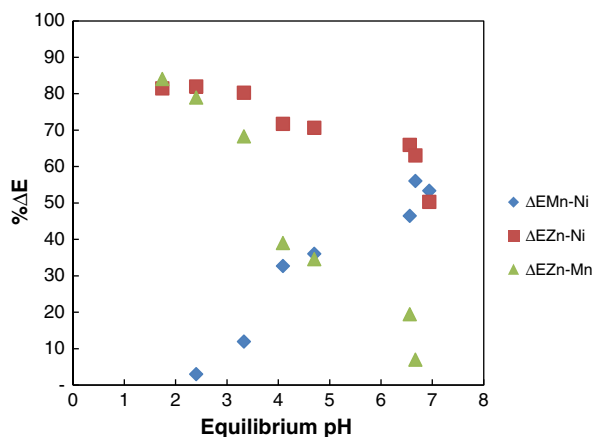
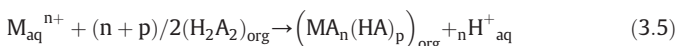


Fig. 5. Extraction differences for various elements in the second preliminary test (initial aqueous phase concentration: 40 g/L Ni, 20 g/L Mn and 10 g/L Zn; O/A = 1, organic phase: 2.42 M Cyanex 272 in n-dodecane).

factors β . The optimum pH value for separation of Zn/Ni and Zn/Mn is about 2. On the other hand, there is not a good separation of Mn and Ni as shown in Figs. 5 and 6. The results obtained in the first and in the second test suggest that to extract manganese and zinc from leaching solutions D2EHPA diluted in n-dodecane is necessary, since this extractant is much more efficient in selective extraction of manganese and zinc over nickel. The results of preliminary tests showed that the best organic liquid was D2EHPA and the results of the first experiment were used to determine the real stoichiometric concentration of D2EHPA. The calculation of real moles was carried out by slope analysis.

3.2.2. Calculate of real moles of D2EHPA: slope analysis

Several equilibrium models for solvent extraction of metals by D2EHPA have been proposed in the literature (Kumar et al., 2009; Mansur et al., 2002; Sainz-Diaz et al., 1996; Vegliò and Slater, 1996). Kumar et al. (2009) for example suggest the reaction of extraction of the metal ion with D2EHPA as follows:



where H_2A_2 is the extractant in dimeric form, M is metal, n is valence of the metal or metal complex ion and p is the number of molecules of extractant engaged in reaction. K, the equilibrium constant of reaction, is calculated as follows:

$$K = \frac{[MA_n(HA)_p]_{org} [H^+]_{aq}^n}{[M^{n+}]_{aq} [H_2A_2]_{org}^{(n+p)/2}} \quad (3.6)$$

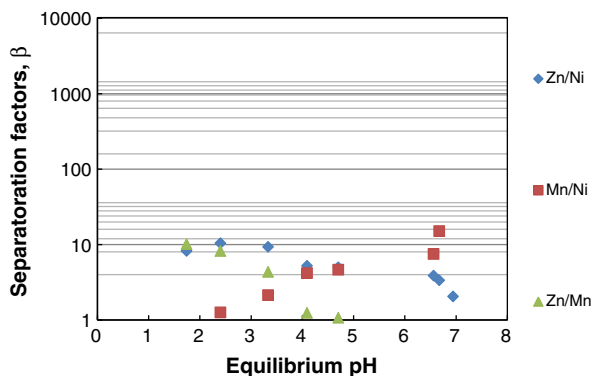


Fig. 6. Separation factors against pH for the second preliminary test (initial aqueous phase concentration: 40 g/L Ni, 20 g/L Mn and 10 g/L Zn; O/A = 1, organic phase: 2.42 M Cyanex 272 in n-dodecane).

This mechanism describes the extraction of single metal ion (for example only Zn) with D2EHPA. The reaction (3.5) is more specific than Eq. (3.1) but still does not consider the other factors that influence the extraction mechanism, for example the resistances of the transfer and the influences of possible intermediate complexes (metal ions–other metal ions) not extractable.

The generic reaction (3.7) was considered to determine the moles of D2EHPA for extraction of metals:



where

$M_{f.a.}$ metallic species (Zn/Mn/Ni);
 RH extractant (D2EHPA) in organic phase;
 n number of moles;
 $MR_{f.o.}$ metallic species in organic phase.

To determine exact real moles of D2EHPA in the experimental conditions investigated with real concentrations of metals in the aqueous phase, the distribution ratio of each metals is considered:

$$\log D = \log K + n \log [RH] + npH \quad (3.8)$$

where

D distribution ratio of metal;
 K equilibrium constant of reaction.

The results obtained from the first experiment with D2EHPA (2.42 M) are used to draw graphs with logD versus pH. Fig. 7 shows the trend of logD as a function of the pH for Zn, Mn and Ni. Table 2 summarizes the results obtained by slope analysis. As it can be noted, the experimental data are well arranged on the straight line and R^2 are greater than 0.9. R^2 is the coefficient of linear correlation: if coefficient is close to 1 the regression analysis is well done, i.e. the mathematical model well fits experimental data.

3.2.3. Solvent extraction tests: determination of the best conditions to extract Mn and Zn

Several tests were carried out to determine the best conditions for extraction of Mn and Zn from aqueous phase. The aim of this series of experiments was to investigate the trend of extraction of metals by changing three factors: % v/v of D2EHPA (10–55% v/v) in n-dodecane, O/A volume ratio (0.5–1.5) and pH (1–5) of extraction. In each test concentrations of metals were 40 g/L Ni, 20 g/L Mn and 10 g/L Zn. Table 3 describes the conditions and the results of these experiments. For each test the volume of aqueous phase was 50 mL and the volume of organic liquid depended on the ratio O/A required for each test of the experimental plan. A regression analysis was carried out to derive a useful tool able to calculate nickel, manganese and zinc extraction yields even for conditions not directly tested. The results of regression analysis were the following:

$$Y_{Ni}(\%) = 7.80X_3 + 4.05X_2^3 + 0.025X_1^2 - 0.049X_2X_1^3 - 0.771X_3^2, \quad R^2 = 0.88 \quad (3.9)$$

$$Y_{Mn}(\%) = 1.94X_1X_2X_3 + 63.73X_2 - 3.64X_1X_2^2 - 22.53X_3 - 0.039X_1^2X_3, \quad R^2 = 0.98 \quad (3.10)$$

$$Y_{Zn}(\%) = -161.58 + 221.46X_3 - 61.78X_3^2 + 5.61X_3^3 + 5.40 \cdot 10^{-5}X_1^3, \quad R^2 = 0.91. \quad (3.11)$$

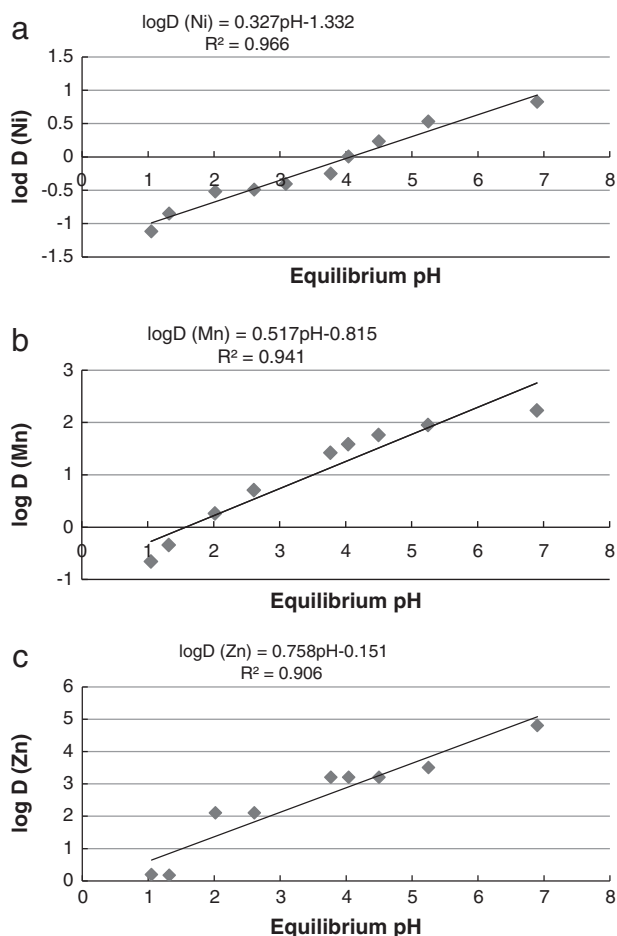


Fig. 7. Slope analysis to calculate real stoichiometric mole of D2EHPA. Figure (a) for nickel, figure (b) for manganese and figure (c) for zinc.

Where X_1 , X_2 and X_3 are % v/v of D2EHPA in n-dodecane, O/A volume ratio and pH, respectively and Y is the extraction yield of the specific element. Comparison between the experimental extraction yields of Ni, Mn and Zn and those obtained using equations above is shown in the scatter diagram. Fig. 8 shows the scatter diagram for those three metals. The experimental data are well fitted for Mn and Zn by Eqs. (3.10) and (3.11) as also shown by values of correlation coefficient R^2 ($R^2 = 0.91$ for zinc extraction and $R^2 = 0.98$ for Mn extraction). Data are fitted quite well even for Ni, as R^2 is 0.88. These mathematical models are used to determine the experimental conditions to extract Mn and Zn and to minimize the extraction of Ni. The best values of factors are 10–30% v/v of D2EHPA in n-dodecane, 0.5–1.5 of O/A volume ratio and 2–3 of pH. D2EHPA greater than 30% v/v was not chosen because in a hypothetical industrial application it should be preferable to use low quantities of extractant for economical and safety reasons. The values for O/A were selected to find the best ratio of volume with the

Table 2

Stoichiometric moles (n) of D2EHPA to extract each element and equilibrium constant of the reactions.

Slope analysis: $\log D = \log K + n \log [RH] + npH$					
Ni:		Mn:		Zn:	
$\log D (Ni) =$		$\log D (Mn) =$		$\log D (Zn) =$	
0.3273pH – 1.3324		0.5175pH – 0.8153		0.7583pH – 0.1513	
n	0.327	n	0.518	n	0.758
K	0.016	K	0.097	K	0.360

Table 3

Experimental data of the second series of solvent extraction tests to investigate the % of extraction of Mn, Zn and Ni varying several parameters.

Test	% v/v D2EHPA	O/A volume ratio	pH	% Ni extraction	% Mn extraction	% Zn extraction
1	10	1.5	1.38	15.81	24.88	59.53
2	10	1.5	1.73	22.50	–	72.65
3	10	1.5	2.65	25.69	27.95	99.22
4	10	1.5	3.66	25.00	36	99.26
5	10	1.5	4.65	26.35	–	–
6	10	1.5	4.94	–	44	99.70
7	15	1.5	1.30	12.25	1.37	24.53
8	15	1.5	1.57	–	3.00	46.85
9	15	1.5	1.95	13.00	12.88	87.24
10	15	1.5	3.30	22.06	39.81	99.43
11	15	1.5	4.11	19.95	57.69	99.81
12	15	1.5	4.80	24.65	72.88	99.86
13	20	1	1.34	4.13	–	15.98
14	20	1	1.60	–	12.63	45.80
15	20	1	2.07	6.25	–	–
16	20	1	3.36	9.25	32.55	98.62
17	20	1	4.06	14.06	50.19	99.64
18	35	0.5	1.19	8.19	9.75	39.98
19	35	0.5	2.36	18.00	–	89.95
20	35	0.5	3.38	17.13	26.60	98.73
21	35	0.5	4.68	–	–	99.60
22	55	0.5	1.35	5.12	9.75	47.90
23	55	0.5	1.62	16.50	–	73.65
24	55	0.5	2.07	–	17.13	98.90
25	55	0.5	2.5	16.25	25.30	97.54
26	55	0.5	3.65	17.00	54.25	99.54
27	55	0.5	4.25	22.65	63.31	99.51

aim to minimize the volume of organic phase (O/A=0.5) when extracting the maximum was sufficient to extract metals quantity of Mn and Zn. Values O/A greater than 1.5 were not selected because in previous tests a third phase between organic and aqueous solutions formed. This third phase probably adversely affected the extraction of metallic ions. The pH range for extraction of Mn and Zn was selected to be 2–3 as indicated by a preliminary test carried out on the aqueous phase.

Table 4 summarizes the best operating conditions which could be identified from mathematical Eqs. (3.9), (3.10) and (3.11). It can be noted that 20% and 30% v/v of D2EHPA minimize the extraction of nickel; 20% v/v of extractant should be selected for economical and safety considerations. In experimental tests carried out with O/A volume ratio equal to 1.5 a third phase between organic and aqueous solutions occurred and grew with increasing of pH. This third phase could have effects of slowing or even block the transfer of metals from pH 2–3 does not have a significant effect on the % of extraction. Confirming the data of preliminary tests pH 2–2.5 was selected as best pH range.

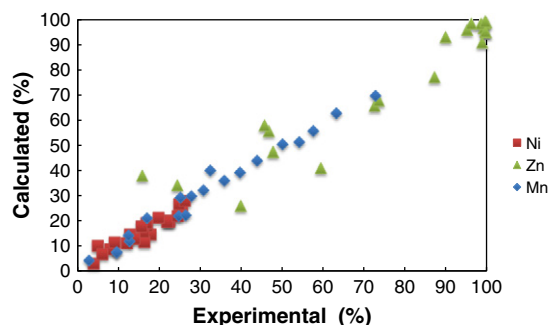


Fig. 8. Scatter diagram of the experimental extraction yields and those calculated for Ni, Mn and Zn.

Table 4

Better conditions to extract Mn and Zn from aqueous phase calculated by models (3.9), (3.10) and (3.11).

pH	% v/v D2EHPA	O/A volume ratio	% Ni extraction	% Mn extraction	% Zn extraction
2	20	1	6.9	20.4	79.5
2	30	1	−5.1	18.9	80.6
2.5	20	1	9.1	27.7	94.1
2.5	30	1	−2.9	34.9	95.1
2.5	20	1.5	8.9	17.1	94.1
3	20	1	10.9	35.1	98.7
3	30	1	−1.1	51	99.8
3	20	1.5	10.7	34.1	98.7

The best operating conditions to maximize the extraction of Mn and Zn and to minimize the extraction of Ni are:

- pH = 2–2.5;
- 20% v/v D2EHPA in n-dodecane;
- O/A volume ratio = 1.

These conditions were adopted for solvent extraction test.

3.2.4. Solvent extraction

Solvent extraction tests were carried out with D2EHPA (20% v/v) in n-dodecane and at pH less than 2.5 because the results of preliminary test showed that these were the more efficient conditions to extract Mn and Zn from aqueous phase. The experimental temperature was set at 25 °C. A solvent extraction experiment was carried out in three stages, as three steps were assumed to be sufficient to separate Mn and Zn, and aqueous phase was put in contact with fresh organic phase (20% v/v D2EHPA in n-dodecane, O/A = 1) at each stage.

Table 5 shows the results obtained stage by stage. The extraction yields for zinc and manganese are very high but for nickel it is about 10% for each stage.

Data for the first stage are similar to those expected from the mathematical models and this confirms that relations (3.9), (3.10) and (3.11) describe well the extractions of the metals in the conditions investigated.

The results of this test suggest that two steps are adequate to extract 100% Zn, 95% Mn and whereas the residual aqueous phase contains about 80% of Ni. Total organic phase has the compositions of 5 g/L Zn, 9.5 g/L Mn and 4 g/L Ni (the volume of the total organic solution is double of aqueous liquid because two fresh organic phase are mixed); the residual aqueous liquid contains 0 g/L Zn, 1 g/L Mn and 32 g/L Ni.

3.3. Stripping tests

In the first stripping 2 M sulfuric acid solution was used, O/A volume ratio was 1 and four stages of stripping were used, whereas in the second test 4 M sulfuric acid solution was used, O/A volume ratio 2 and two steps of stripping. For each stage the organic phase containing metals was mixed with fresh sulfuric acid solution after separation of the two phases. The results of the first stripping test are shown in Table 6. From results of extraction experiments the initial concentrations of metals were 4 g/L Ni, 9.5 g/L Mn and 5 g/L Zn

Table 5

% Extraction for zinc, manganese and nickel stage by stage (initial aqueous phase concentration: 40 g/L Ni, 20 g/L Mn and 10 g/L Zn; organic phase: 20% v/v D2EHPA in n-dodecane, O/A v/v = 1).

Stage	pH	% Zn extraction	% Mn extraction	% Ni extraction
I	2.22	88.15	21.13	11.23
II	2.41	99.62	95.65	22.21
III	2.44	99.99	99.15	32.69

Table 6

% Stripping for zinc, manganese and nickel during the first stripping test (initial organic phase concentration: 4 g/L Ni, 9.57 g/L Mn and 4.98 g/L Zn; stripping solution for each stage: sulfuric acid solution 2 M, O/A v/v = 1).

Stage	pH	% Zn stripping	% Mn stripping	% Ni stripping
I	0.39	93.26	78.60	97.85
II	0.37	97.66	99.17	99.93
III	0.33	99.88	99.40	99.99
IV	0.33	99.98	99.96	99.99

and in organic phase, whereas after stripping manganese was about 0.01 g/L, zinc and nickel are <0.01 g/L.

The stripping yields are >99% for all metals. The results of the second experiment are shown in Table 7. In organic phase, after stripping, manganese is about 0.19 g/L, zinc <0.01 g/L and nickel is 0.02 g/L. The stripping yields are very high and greater than 99% for Ni and Zn and about 98% for Mn. Summarizing the results, the use of higher concentrations of sulfuric acid solution can reduce the number of stages and gives a lower amount of aqueous solution as a result.

4. Process analysis

According to experimental results obtained in the experimental campaign a possible process for treatment of NiMH spent batteries was developed. Fig. 9 shows the block diagram proposed. In the process lanthanum and cerium could be recovered and two solutions could be collected out. The first solution is rich in nickel and some traces of other metals like zinc and manganese and it is assumed that this phase could be sent to a section for recovery of nickel. The second liquid output contains manganese, zinc and a small amount of nickel lost from the first solution. It is proposed that the solution could be sent to an alkaline and zinc carbon spent batteries treatment section. The process for recovery of metals from alkaline and zinc carbon spent batteries has already been studied in previous works (Ferella et al., 2010; Furlani et al., 2009; Sayilgan et al., 2009) and it includes at the end of the process a section of recovery of manganese and zinc by electrolysis. For this reason it is assumed that the Mn and Zn rich solution leaving the stripping step can be sent to electrolytic section of process for recycling of alkaline and zinc carbon spent batteries. The steps of the process are:

- washing of initial NiMH spent batteries powder to remove soluble compounds like KOH and chlorine compounds. The washing could be carried out using 20% pulp density at room temperature for 1 h;
- first leaching of the powder with 2 M sulfuric acid solution at high temperature (80–90 °C), 15% pulp density for 3 h. In this step majority of metals and about 35% of La and Ce are dissolved;
- second leaching of solid residue with 1 M sulfuric acid, 15% pulp density at room temperature for 1 h. The goal of this second leaching is to dissolve almost completely La and Ce;
- precipitation step with NaOH until pH of 1.6 to precipitate and recover La and Ce. The recover yields of rare earths are estimated about 99%;
- liquid–liquid extraction with D2EHPA (20% v/v) in organic solvent like kerosene or n-dodecane in two stages to obtain refined rich in Ni with traces of Mn and Zn. This solution is sent to a step to recover nickel;

Table 7

% Stripping for zinc, manganese and nickel during the second stripping test (initial organic phase concentration: 4 g/L Ni, 9.57 g/L Mn and 4.98 g/L Zn; stripping solution for each stage: sulfuric acid solution 4 M, O/A v/v = 2).

Stage	pH	% Zn stripping	% Mn stripping	% Ni stripping
I	0.13	98.93	94.08	91.61
II	0.03	99.90	97.98	99.51

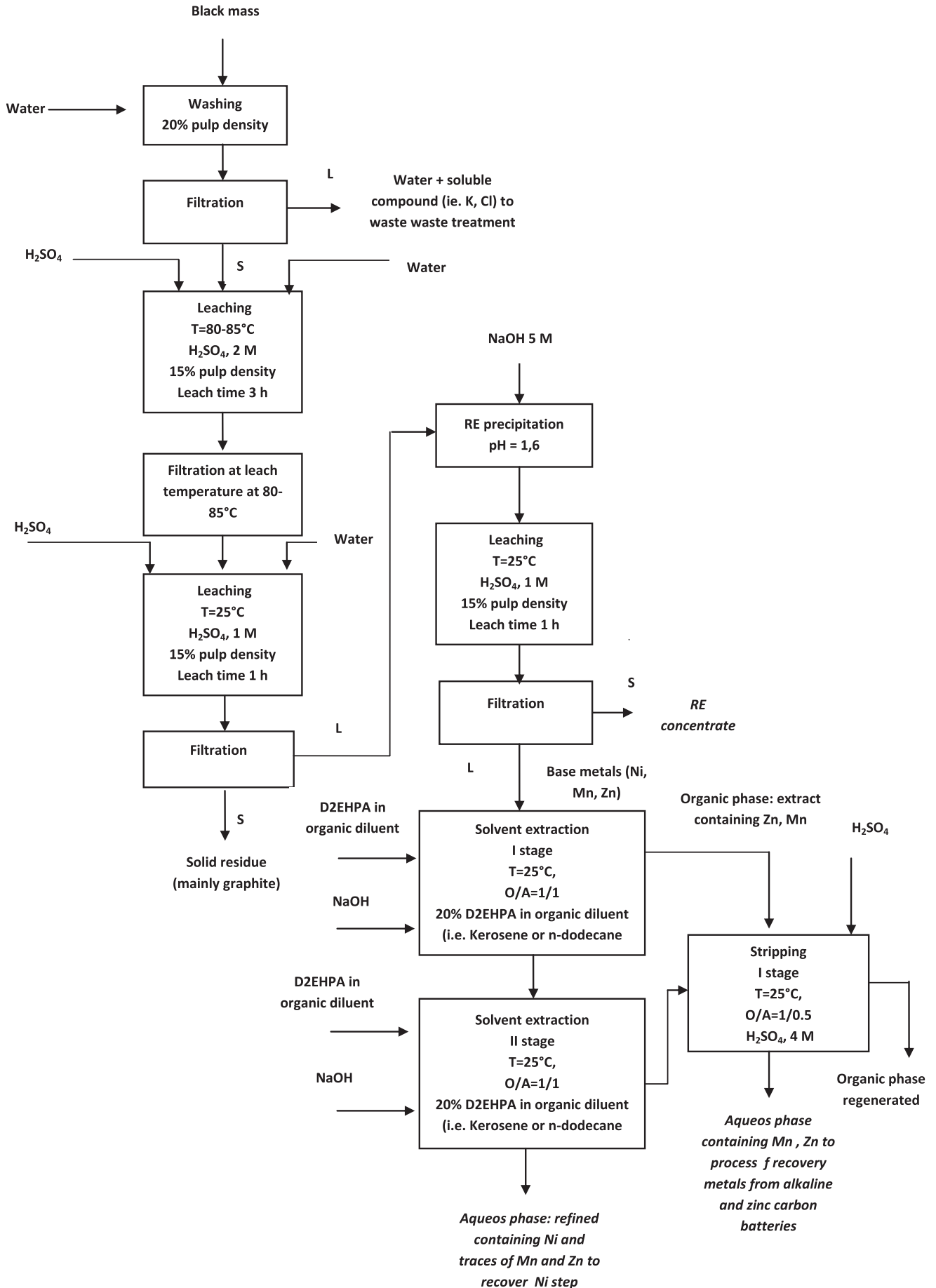


Fig. 9. Block diagram for the recovery of rare earths from NiMH spent batteries and for separation of base metals (Ni, Mn and Zn).

- stripping of organic phase with 4 M sulfuric acid solution for removal Mn and Zn from organic liquid. The organic liquid after stripping is regenerated and could be used again for another liquid–liquid extraction step. The aqueous phase rich in Mn and Zn and some residual Ni could be sent to electrolytic section of a process for recycling of alkaline and zinc carbon spent batteries.

5. Conclusions

The characterization of NiMH spent batteries showed that Ni, Mn and Zn were the most concentrated metals in this type of batteries, but also important were La and Ce (about 29% Ni, 13% Mn, 8% Zn, 5% La and 2% Ce). The previous tests described in our previous work (Innocenzi and Vegliò, 2012) suggested that RE could be recovered by precipitation after leaching process with sulfuric acid. The results of precipitation showed that La and Ce could be recovered at 95% and the solid precipitated had 89–91% purity. The tests also showed that the precipitation process is not efficient to selectively recover the other metals (Mn, Ni, Zn) dissolved so that solvent extraction is adopted to separate manganese and zinc from leaching solution process of NiMH spent batteries. The solutions used in solvent extraction tests are pregnant solutions and have about 40 g/L of Ni, 20 g/L of Mn and 10 g/L of Zn. These solutions simulate the concentration of real solutions coming from leaching and further precipitation of RE. D2EHPA and Cyanex 272 in n-dodecane were investigated as extractant and the results of preliminary tests showed that D2EHPA (20% v/v) is more efficient to extract manganese and zinc than Cyanex 272.

It is possible to conclude that:

- The order of extraction is $Zn > Mn > Ni$.
- Two stages of extraction are enough to remove Zn and Mn. The conditions for each step are $O/A = 1/1$, room temperature, about 30 min to reach equilibrium and $pH \leq 2.5$. In these conditions around 100% of Zn, 95% of Mn and 20% of Ni are extracted; the total organic phase (sum of two organic liquids) has 4.98 g/L of Zn, 9.57 g/L of Mn and 4 g/L of Ni. The residual aqueous phase has about 0.038 g/L of Zn, 0.87 g/L of Mn and 32 g/L of Ni: this phase is purified from zinc and contains a small quantity of manganese.
- Stripping tests demonstrate that sulfuric acid solution is very efficient to remove metals from organic phase and one stage of stripping is enough if 4 M sulfuric acid solution is used with O/A volume ratio equal to 2.
- The stripping yields are very high: 99% Zn, 94% Mn and 92% Ni whereas the aqueous phase contains 9.86 g/L Zn, 18 g/L of Mn and around 7.33 g/L of Ni. The residual organic phase after stripping contains 0.05 g/L of Zn, 0.57 g/L of Mn and 0.33 g/L of Ni. This liquid could be reused for another extraction step.

In conclusion, from these results it can be inferred that a suitable recovery process provides 2 stages of extraction with 20% v/v of D2EHPA in n-dodecane ($O/A = 1/1$, room temperature, 30 min of contact, $pH \leq 2.5$) and one stage of stripping with 4 M H_2SO_4 solution ($O/A = 1/0.5$, room temperature, 15 min of contact) from which two liquid phases are obtained. The refined could be treated to recover Ni for example by precipitation, whereas the second liquid rich in Mn and Zn could be sent to an electrolytic section of alkaline and zinc carbon spent batteries.

A possible future work will be aimed at minimization of the co-extraction of Ni to lose less nickel during extraction of manganese and zinc.

Acknowledgments

The authors acknowledge Mrs Fabiola Ferrante and Marcello Centofanti for their assistance in XRF characterization and AAS analysis. The authors especially thank the Cytec company for giving a free sample of Cyanex 272 that was carried out in the experiments.

References

- Devi, N.B., Nathsarma, K.C., Chakravorty, V., 1997. Extraction and separation of Mn(II) and Zn(II) from sulphate solutions by sodium salt of Cyanex 272. *Hydrometallurgy* 45, 169–179.
- Ferella, F., De Michelis, I., Beolchini, F., Innocenzi, V., Vegliò, F., 2010. Extraction of zinc and manganese from alkaline and zinc–carbon spent batteries by citric–sulphuric acid solution. *Hindawi Publishing Corporation. Int. J. Chem. Eng.* 2010 <http://dx.doi.org/10.1155/2010/659434> (Article ID 659434, 13 pages).
- Flett, D.S., 2005. Solvent extraction in hydrometallurgy: the role of organophosphorus extractants. *J. Organomet. Chem.* 690, 2426–2438.
- Fontana, D., Pietrelli, L., 2009. Separation of middle rare earths by solvent extraction using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester as an extractant. *J. Rare Earths* 27 (5), 830.
- Furlani, G., Moscardini, E., Pagnanelli, F., Ferella, F., Vegliò, F., Toro, L., 2009. Recovery of manganese from zinc alkaline batteries by reductive acid leaching using carbohydrates as reductant. *Hydrometallurgy* 99, 115–118.
- Innocenzi, V., Vegliò, F., 2012. Recovery of rare earths and base metals from spent nickel-metal hydride batteries by sequential sulphuric acid leaching and selective precipitation. *J. Power Sources* 211, 184–191.
- Kongolo, K., Mwema, M.D., Banza, A.N., Gock, E., 2003. Cobalt and zinc recovery from copper sulphate solution by solvent extraction. *Miner. Eng.* 16, 1371–1374.
- Kumar, V., Kumar, M., Kumar, Jha M., Jeong, J., Lee, J., 2009. Solvent extraction of cadmium from sulfate solution with di-(2-ethylhexyl) phosphoric acid diluted in kerosene. *Hydrometallurgy* 96, 230–234.
- Li, L., Xu, S., Ju, Z., Wu, F., 2009. Recovery of Ni, Co and rare earths from spent Ni-metal hydride batteries and preparation of spherical $Ni(OH)_2$. *Hydrometallurgy* 100, 41–46.
- Long, H., Chai, L., Qin, W., Tang, S., 2010. Solvent extraction of zinc from zinc sulfate solution. *J. Cent. South Univ. Technol.* 17, 760–764.
- Mansur, M.B., Slater, M.J., Biscaila Jr., E.C., 2002. Equilibrium analysis of reactive liquid–liquid test system $ZnSO_4/D2EHPA/n$ -heptane. *Hydrometallurgy* 63, 117–126.
- Reddy, B.R., Neela Priya, D., 2005. Process development for the separation of copper (II), nickel (II) and zinc (II) from sulphate solutions by solvent extraction using LIX 84I. *Sep. Purif. Technol.* 45, 163–167.
- Reddy, B.R., Parija, C., BhaskaraSarma, P.V.R., 1999. Processing of solutions containing nickel and ammonium sulphate through solvent extraction using PC-88. *Hydrometallurgy* 53, 11–17.
- Ritcey, G.M., 2006. Solvent extraction in hydrometallurgy: present and future. *Tsinghua Sci. Technol.* 11 (2), 137–152.
- Rodrigues, L.E.O.C., Mansur, M.B., 2010. Hydrometallurgical separation of rare earth elements, cobalt and nickel from spent nickel-metal-hydride batteries. *J. Power Sources* 195, 3735–3741.
- Sainz-Diaz, C.I., Klocker, H., Marr, R., Bart, H.J., 1996. New approach in the modeling of the extraction equilibrium of zinc with bis-(2 ethylhexyl) phosphoric acid. *Hydrometallurgy* 42, 1–11.
- Sayilgan, E., Kukrer, T., Ferella, F., Akcil, A., Vegliò, F., Kitis, M., 2009. Reductive leaching of manganese and zinc from spent alkaline and zinc–carbon batteries in acidic media. *Hydrometallurgy* 97, 73–79.
- Tsakiridis, P.E., Agatzini, S.L., 2004. Simultaneous solvent extraction of cobalt and nickel in the presence of manganese and magnesium from sulfate solutions by Cyanex 301. *Hydrometallurgy* 72, 269–278.
- Tsakiridis, P.E., Agatzini, S.L., 2005. Solvent extraction of aluminium in the presence of cobalt, nickel and magnesium from sulphate solutions by Cyanex 272. *Hydrometallurgy* 80, 90–97.
- Vegliò, F., Slater, M.J., 1996. Design of liquid–liquid extraction columns for the possible test system $Zn/D2EHPA$ in n-dodecane. *Hydrometallurgy* 42, 177–195.
- Zhang, P., Yokoyama, T., Itabashi, O., Wakui, Y., Suzuki, T.M., Inoue, K., 1998. Hydrometallurgical process for recovery of metal values from spent nickel-metal hydride secondary batteries. *Hydrometallurgy* 50, 61–75.
- Zhang, P., Yokoyama, T., Itabashi, O., Wakui, Y., Suzuki, T.M., Inoue, K., 1999. Recovery of metal values from spent nickel-metal hydride rechargeable batteries. *J. Power Sources* 77, 116–122.